A Study of the Mineralogy of the Lower Kittanning Underclay in the Vicinity of Oak Hill, Ohio

By

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CHAPTER I

INTRODUCTION

The Middle Pennsylvanian series is comprised in part by the Allegheny Group, the members of which contain extensive coal and clay deposits in Ohio and surrounding states. Stratigraphically, the Lower Kittanning Underclay is located at the top of the lower one-third portion of the Allegheny Group. Within this group, several repetitive sequences of a marine or brackish-water unit overlying a coal deposit have been recognized. Wanless and Weller (1932) denoted each of these successions as separate cyclothems, and divided them into marine and continental subtypes. For instance, the Lower Kittanning sandstone, coal, and underclay (continental) overlain by the Hamden Limestone (marine), exemplifies such a cyclothem.

Alternatively, Pennsylvanian cyclothems can be interpreted as coarsening-upward sequences. In general, these sequences include a marine limestone or shale overlain by a sandstone or sandy shale capped by a coal and underclay. A stratigraphic column of the Pennsylvanian-Permian systems of Ohio (Johnson, 1982) shows that the Lower Kittanning sandstone, coal, and underclay are situated above the Vanport Limestone (Fig. 1). Ferm (1970) has proposed a fluvio-deltaic model for Allegheny cyclothems to explain the coarsening-upward trends. Under this model, the Lower Kittanning sandstone would represent

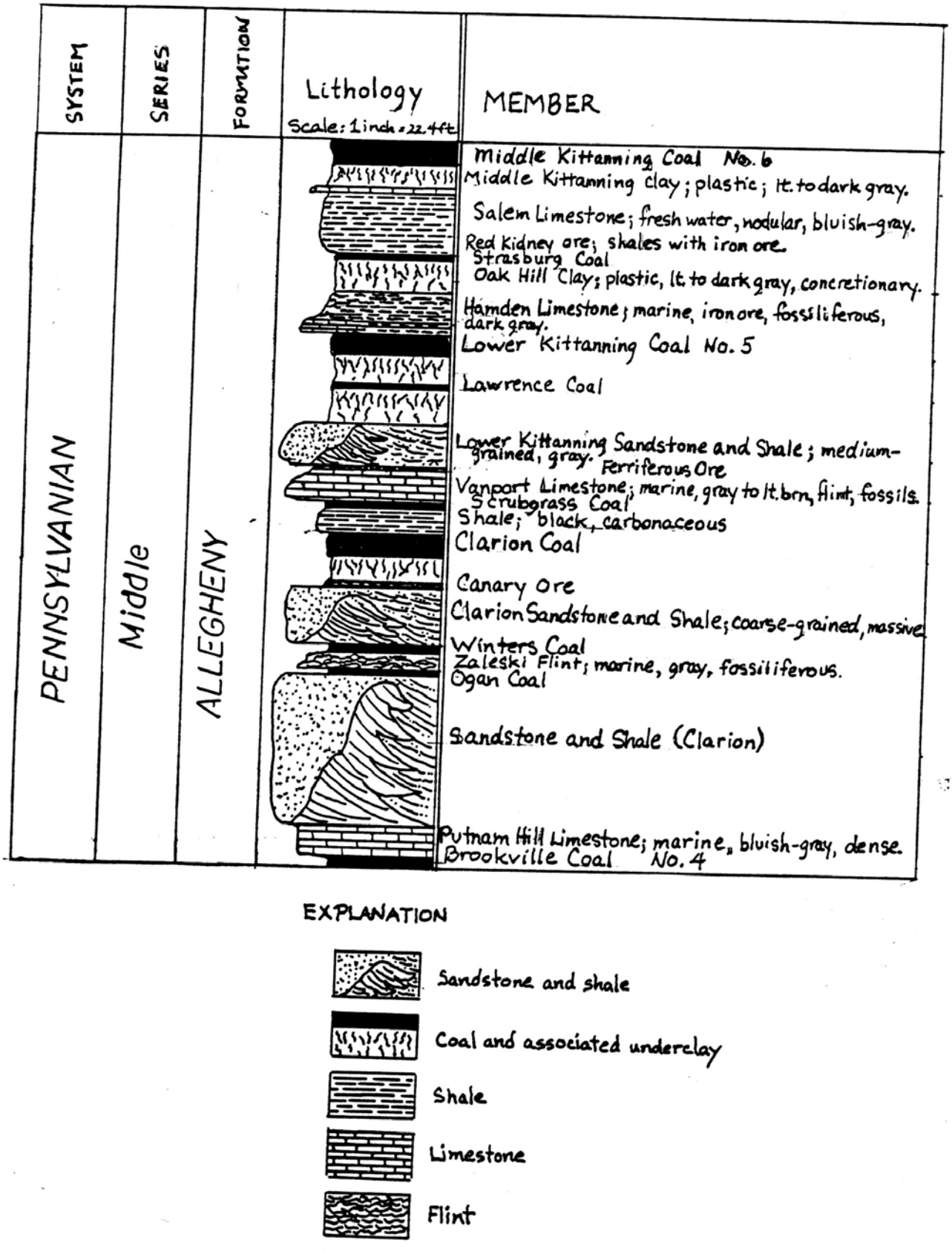

Figure 1 Generalized stratigraphic section of the Lower portion of the Allegheny Group. (From Johnson, 1982)

an active, prograding lobe of a delta, whereas the Lower Kittanning coal and underclay would have developed on an inactive delta lobe. Repetition of the sedimentary sequences implies relatively rapid shifts in position of the prograding delta lobes.

Inactive delta lobes are ideal locations for the accumulation of vegetation in swampy or lagoonal environments. It is easy to imagine the formation of coal members through compaction and lithification of organics, but the origin of the clays beneath them is not immediately clear. Some authors maintain that underclays are paleosols which once supported the coal-forming vegetation above them (Stout et. al., 1923). This view implies that underclays are residual members, the result of weathering and leaching of minerals contained within the preexisting soils. Opponents to this theory argue that there is little vertical variation in the composition of underclays to substantiate the presence of soil horizons (Schultz, 1958). These workers suggest the idea that the clays were transported from another source and have undergone little mineralogic alteration since the time of deposition.

The question addressing the origin of coal-formation underclays like the Lower Kittanning is beyond the scope of this study. Such an undertaking requires detailed quantitative analysis of numerous samples to determine structural and compositional trends within the underclay.

Regardless of origin, Pennsylvanian underclays are well known for their suitability in the production of refractory ceramics, although this association is not universal (Bates, 1960). The clay samples for this study were extracted from a small southern Ohio strip mine which was last worked in 1959. Material mined from this site was used in the local manufacture of fire brick in the vicinity of Oak Hill, Ohio. According to Raymond Hughes of the Cedar Heights Clay Company, all usable material through and including the purest portion of the Lower Kittanning Underclay was taken from the strip mine (personal communication). The specimens studied thus represent material near the base of the underclay.

In order to analyse the underclay qualitatively, specimens were X-rayed to determine their mineralogy. Samples were taken from several locations within the stripped area and in one instance, at varying depths. The purpose was to compare the results with those of other workers and to determine the differences, if any, between the local specimens. Another factor which motivated this research is that my family comes from this sector of Ohio and hence I wished to learn more about the local geology.

CHAPTER II

DESCRIPTION OF SAMPLE LOCALITY

Specimens were collected in Jackson county, Ohio from a small strip mine located in the southeast corner of Section 2, Jefferson township, Oak Hill quadrangle (Fig. 2). A soil core sampler was used to extract the samples. The clays had been exposed to the surface since the cessation of mining operations in 1959.

The strip site consists of a flat barren expanse of white underclay occasionally interrupted by small hills. These hills consist of mixed amounts of sandstone, argillaceous material, iron concretions, and fissile sandy shale. The writer believes that these hills were likely formed when overburden was moved aside during mining to expose and recover the refractory material. The "dump hills" frequently display limonitic and/or hematitic staining in marked contrast to the adjacent homogeneous white underclay.

Selenite gypsum was found in two isolated areas in the flat white portion of the strip site. The gypsum occurs in large clear crystals at the surface of the underclay, and in both instances the crystals are distributed within an area of only a few meters.

Of the six specimens obtained from this area, samples 1 through 4 represent material in place near the base of

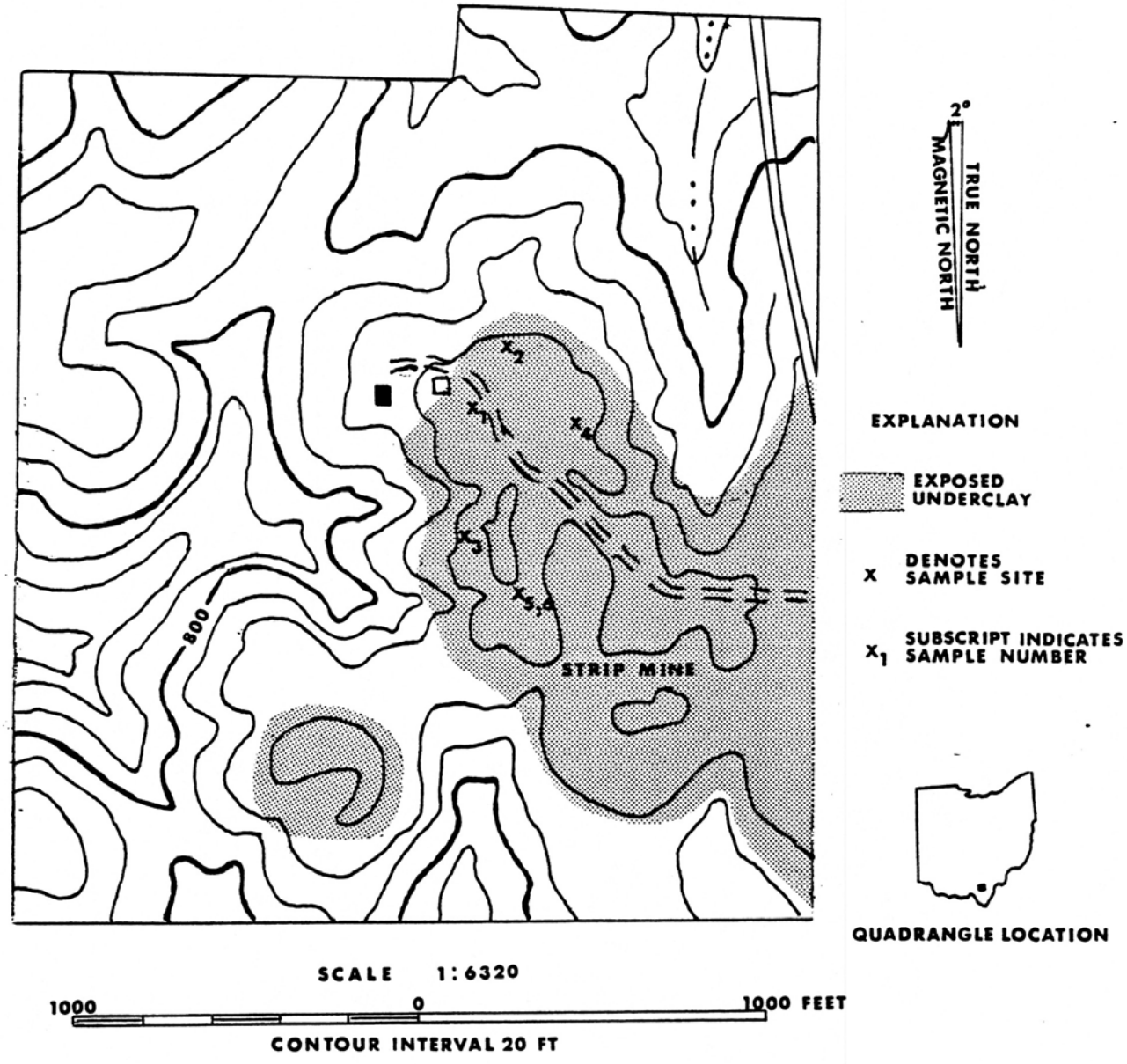

Figure 2 SE 1/4 of Section 2, Jefferson township, Oak Hill quadrangle. Sample locations indicated by x's.

the Lower Kittanning Underclay. Samples 1, 2, and 3 are essentially the same in appearance; all three are light to medium gray, slightly fissile, micaceous, and siliceous. Specimen 4 is comparable to the first three, although it is slightly more sandy and contains larger mica (muscovite) flakes. Since it appears to grade into a sandstone, sample 4 likely represents material at the extreme base of the Lower Kittanning Underclay.

Specimens 5 and 6 were taken from the base of a dump hill, and are quite different in character in hand specimen than the former four. They are finer grained, medium to dark gray, massive, and appear to be less siliceous. Samples 5 and 6 probably do not represent material in place, but were chosen for their contrasting characteristics.

CHAPTER III

EXPERIMENTAL METHODS

Sample Preparation

To determine the whole mineralogic fraction, each clay sample was pulverized by hand to a flour-like consistency using a mortar and pestle. The samples were then front-loaded into an aluminum holder utilizing a glass slide to create a smooth planar surface level with the top of the holder. The slide was also used to brush away excess sample material from the target area before insertion into the diffractometer.

To obtain the clay fraction, each sample was suspended in distilled water to recover particles less than 2μm in diameter. Five percent suspensions by weight were prepared by adding 10 grams of slightly crushed, but not pulverized sample to 200 ml of distilled water in a 250 ml beaker. After agitation with a glass stirring rod, the samples were observed to flocculate, so 2 ml of a 10 percent Calgon solution were added to serve as a dispersing agent. The beakers were then placed into an ultrasonic chamber but flocculation was still observed upon removal from the chamber. Finally, after an additional 2 ml of the Calgon solution were added to the beakers, and each was mixed in a Waring blender for approximately 10 seconds, the suspensions were adequately dispersed.

The time required for 2μm particles to settle the chosen vertical distance of 2 cm was governed by Stoke's Law:

$$t = \frac{18 \cdot n \cdot h \cdot 10^8}{980 \cdot \Delta s \cdot D^2}$$

Where t = settling time (sec)
n = coefficient of viscosity of liquid medium (0.01 poises @ 20 C)
h = settling distance (2 cm)
Δs = difference between particle and liquid densities (1.65 g/cm^3)
D = particle diameter (2μm)

The time calculated according to the equation above was 1 hour, 32 minutes, 45 seconds. After this required interval had elapsed, a 5 ml pipet was inserted into the beakers to a depth of 2 cm, and suspension was drawn from each. This suspension was pipetted onto glass slides and allowed to air dry overnight. Two slides were prepared for each sample to provide a back-up in case of accident.

After obtaining diffraction patterns for the air-dried mounts, the slides were placed into an ethylene-glycol chamber where they remained for a 24-hour period. The purpose of this procedure was to determine the presence of expandable material in the samples.

Heat Treatments

The back-up mount of specimen 2 was heated to 350° C for 24 hours to check for the collapse of expandable material if any was present in the sample.

A second rock-specimen of sample 4 was prepared by the

methods previously described for whole-fraction mounts, and was re-X-rayed to replicate the powder pattern. This sample was then removed from the aluminum holder, placed into a small ceramic crucible, and heated to 600°C for 2 hours. At this temperature, kaolinite should become amorphous, allowing for the determination of trace minerals which would otherwise be obscured by the kaolinite reflections in the diffraction pattern.

Conditions for X-ray Diffraction

A Phillips diffractometer equipped with a strip chart provided the X-ray data for this study. The whole-fraction mounts were run from 4 to 50 degrees 2θ at a goniometer rate of 2 degrees 2θ per minute. The samples were subjected to Cu-K alpha radiation at a power setting of 35 Kv, 15 ma. The chart speed was set at sixty inches per hour. A theta-compensating slit was used to obtain all X-ray diffraction patterns.

The power was readjusted to 35 Kv, 10 ma for the air-dried clay-fraction mounts to prevent the diffraction maxima from going off scale. This adjustment was also necessary for the ethylene-glycol and heat-treated slides. All other conditions were identical to those of the whole-fraction powder mounts.

CHAPTER IV

RESULTS

Whole-Fraction Analysis

The chief constituents common to all six samples include kaolinite, illite, mica (muscovite), and quartz. Powder mounts of specimens 1 through 4 yielded virtually identical X-ray patterns. Furthermore, specimen 1 showed no apparent differences in mineralogy with increasing depth (Fig. 3a).

Samples 5 and 6 showed evidence for the presence of interstratified expandable material in their powder patterns. A broad diffraction peak of the 10 Å phase ranging from approximately 7 to 8.8 degrees 2θ was interpreted to represent such material (Fig. 3b), which was not found in the whole-fraction diffraction patterns of specimens 1 through 4.

Titanium dioxide in the form of the mineral anatase was thought to be present in the specimens, but a heat treatment was necessary to confirm it.

Clay-Fraction Analysis

Owing to the methods employed in preparing sample mounts for clay-fraction analysis, a quantitative assessment of the clay minerals present in the specimens was not possible. For instance, the clay suspensions were agitated when the pipet was inserted to recover the less than 2μm fraction, introducing

experimental error. More importantly, differential settling due to gravity certainly occurred as the suspension on the glass slides was allowed to air dry. Calmer (1971), who utilized the smear mount method for semiquantitative analysis, stressed the importance of producing uniform mounts to obtain replicable X-ray data. Replication is thus a problem even with the best of mounting techniques. With these considerations, the results obtained for this study are qualitative.

Clay-fraction patterns for the glycol-treated specimens are presented in figures 3c, d, e, and f. All glycolated specimens produced X-ray patterns that included an interstratified phase. Specimens 1 and 3 produced identical diffraction patterns, and showed the presence of kaolinite, illite, mica, quartz, and expandable material (Fig. 3c). A comparison of air-dried to glycolated sample for specimen 4 is provided in Figure 3d. Slight shifting in position and broadening of the diffraction peak in the 10 Å range as a result of glycolation was noted for this sample.

The major difference found between the X-ray patterns of samples 1 through 4 and those of specimens 5 and 6 involves the 10 Å interstratified material. The reflections of this material for the latter two samples are broader and weaker than those of the former four (Fig. 3e). Specimens 1 through 4 retain sharper peaks representative of illite/mica reflections after glycolation.

Effects of Heat Treatments

The results of heating the air-dried clay-fraction mount of sample 2 were noted in the diffraction pattern presented in Figure 3f. The 10 Å illite/mica peak sharpened and shifted slightly toward increasing 2θ positions, in contrast to the glycol pattern for the same sample, in which the peak broadened and migrated toward smaller 2θ values. Thus, the interstratified material associated with the illite apparently collapsed as a result of heating to 350°C.

Whole-fraction patterns of sample 4 before and after heating to 600°C confirmed the presence of anatase. Before heating, kaolinite reflections obscured the presence of minor peaks in the X-ray pattern (Fig. 3g). After heating, the kaolinite peaks were diminished, allowing the identification of TiO_2 as anatase (Fig 3h).

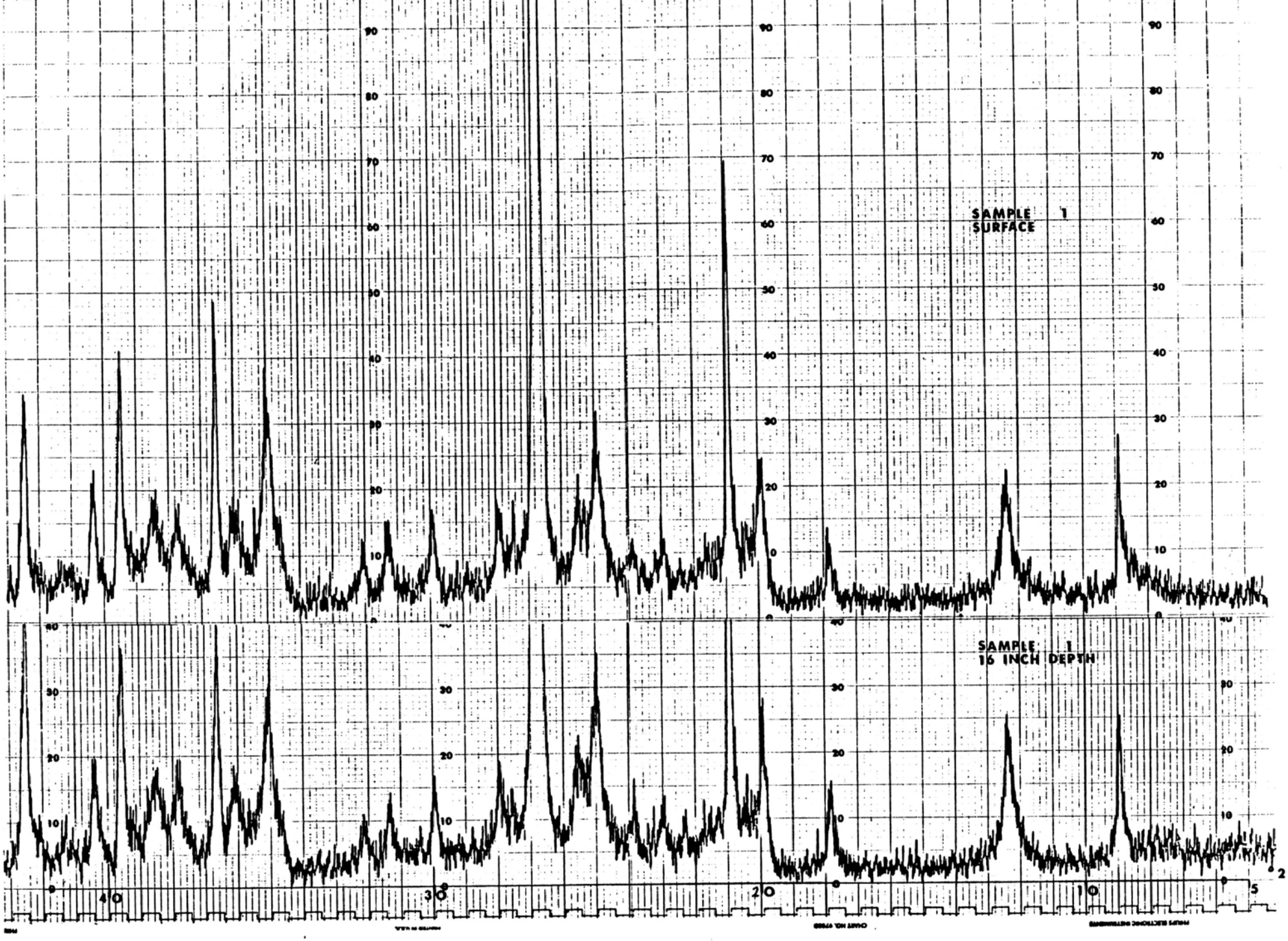

Figure 3a X-ray diffraction patterns for powder mounts of sample 1 at varying depths.

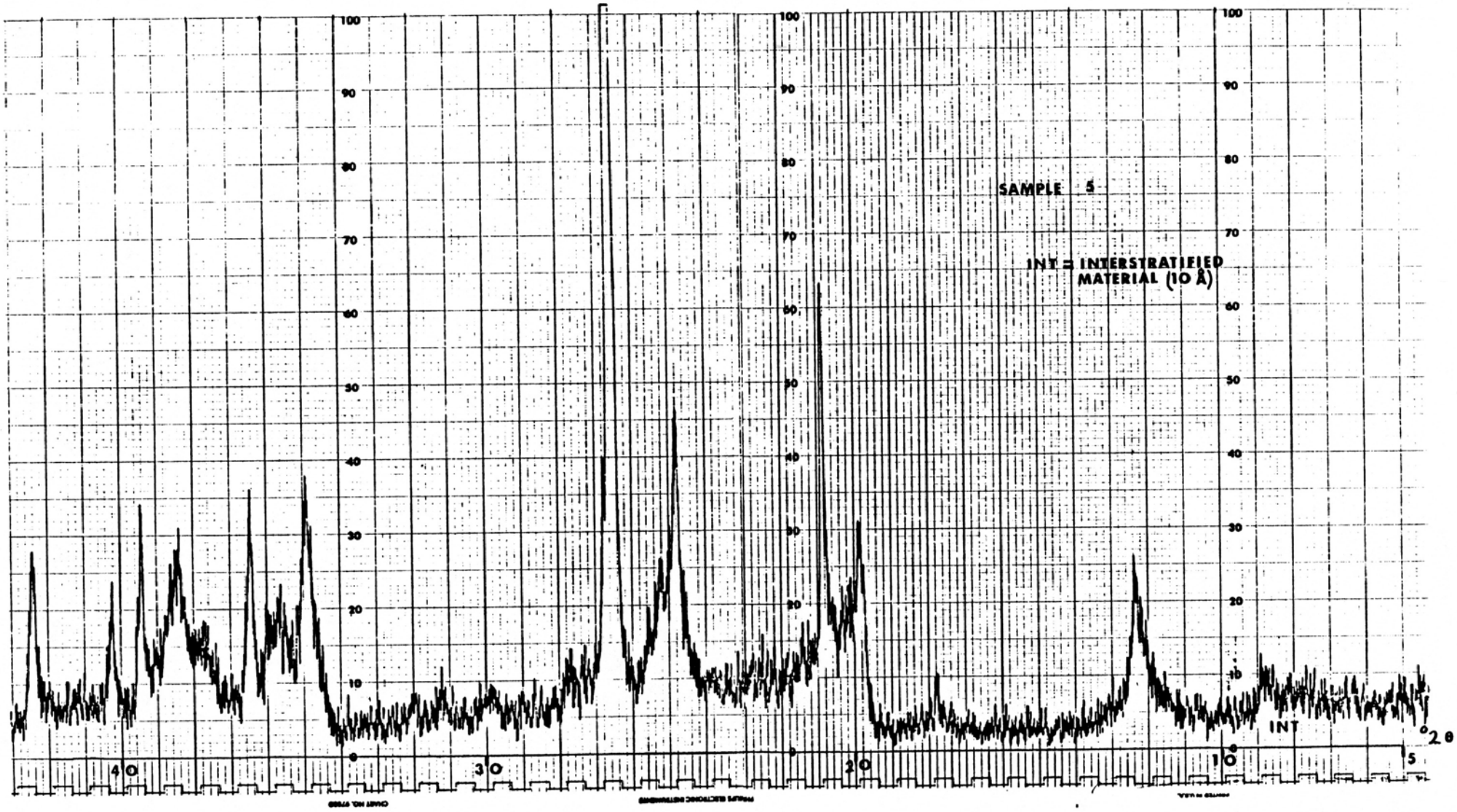

Figure 3b X-ray diffraction pattern for powder mount of sample 5, showing the presence of interstratified material (10 Å).

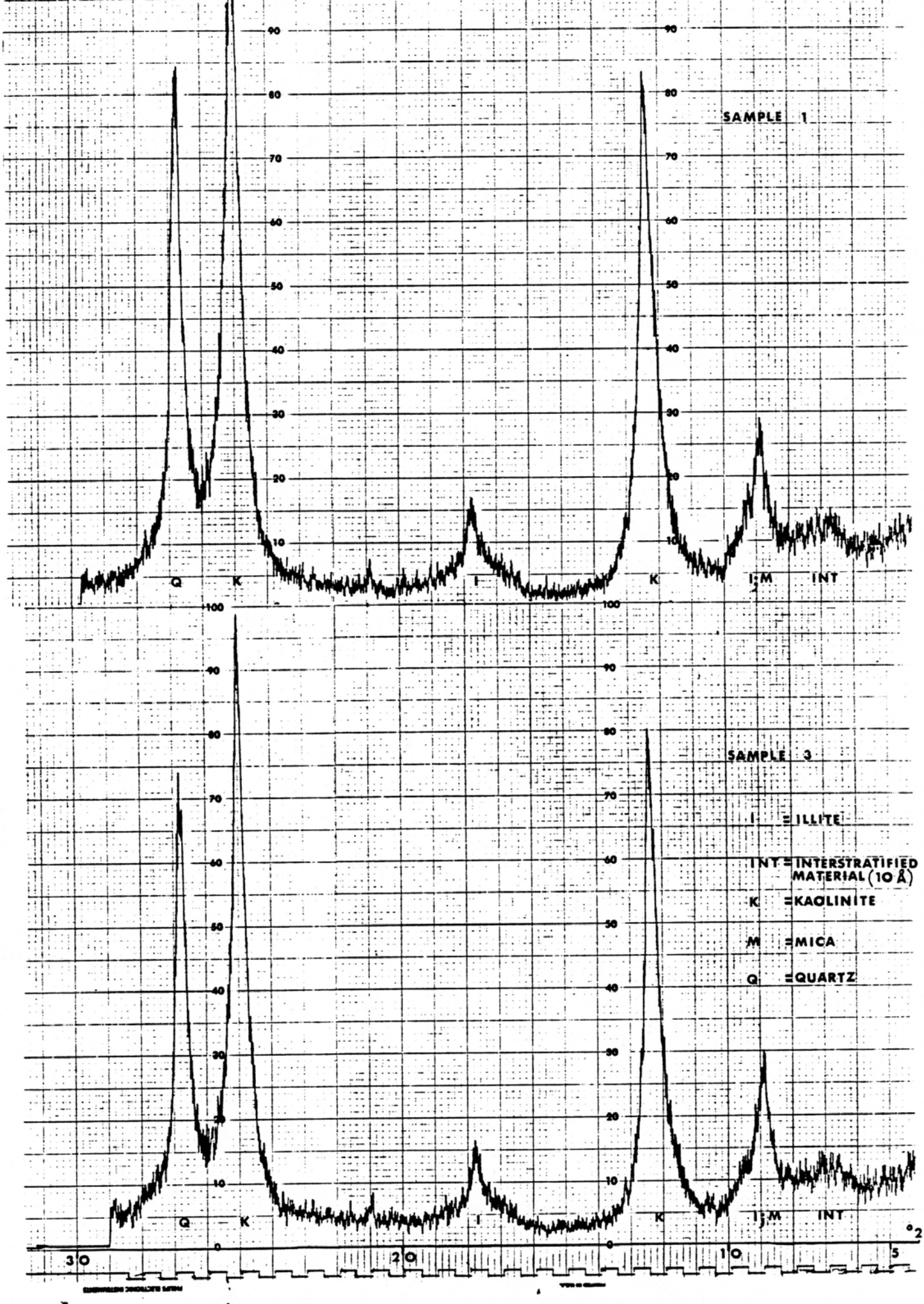

Figure 3c Glycol patterns for Samples 1 and 3.

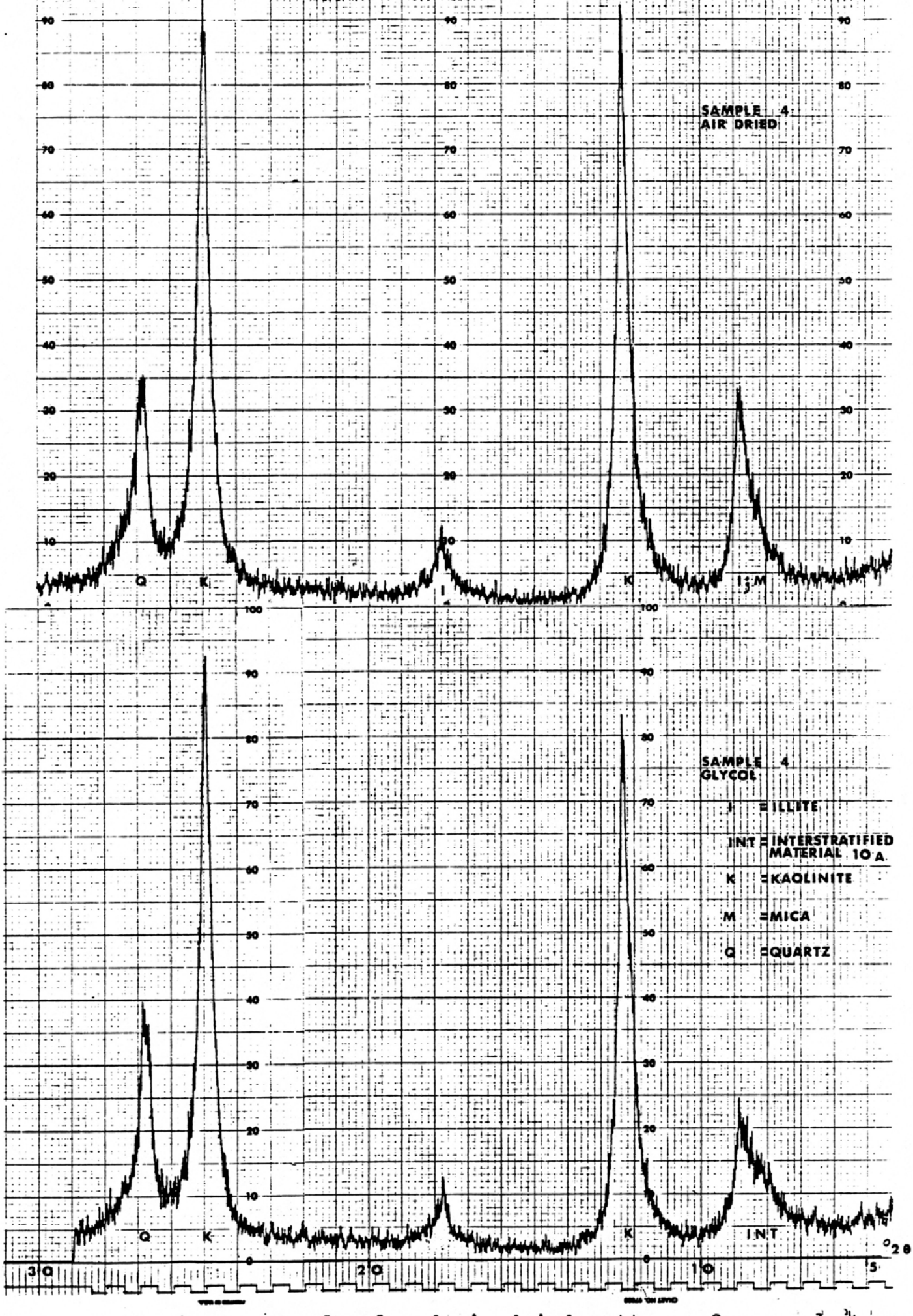

Figure 3d Glycol and air-dried patterns for sample 4.

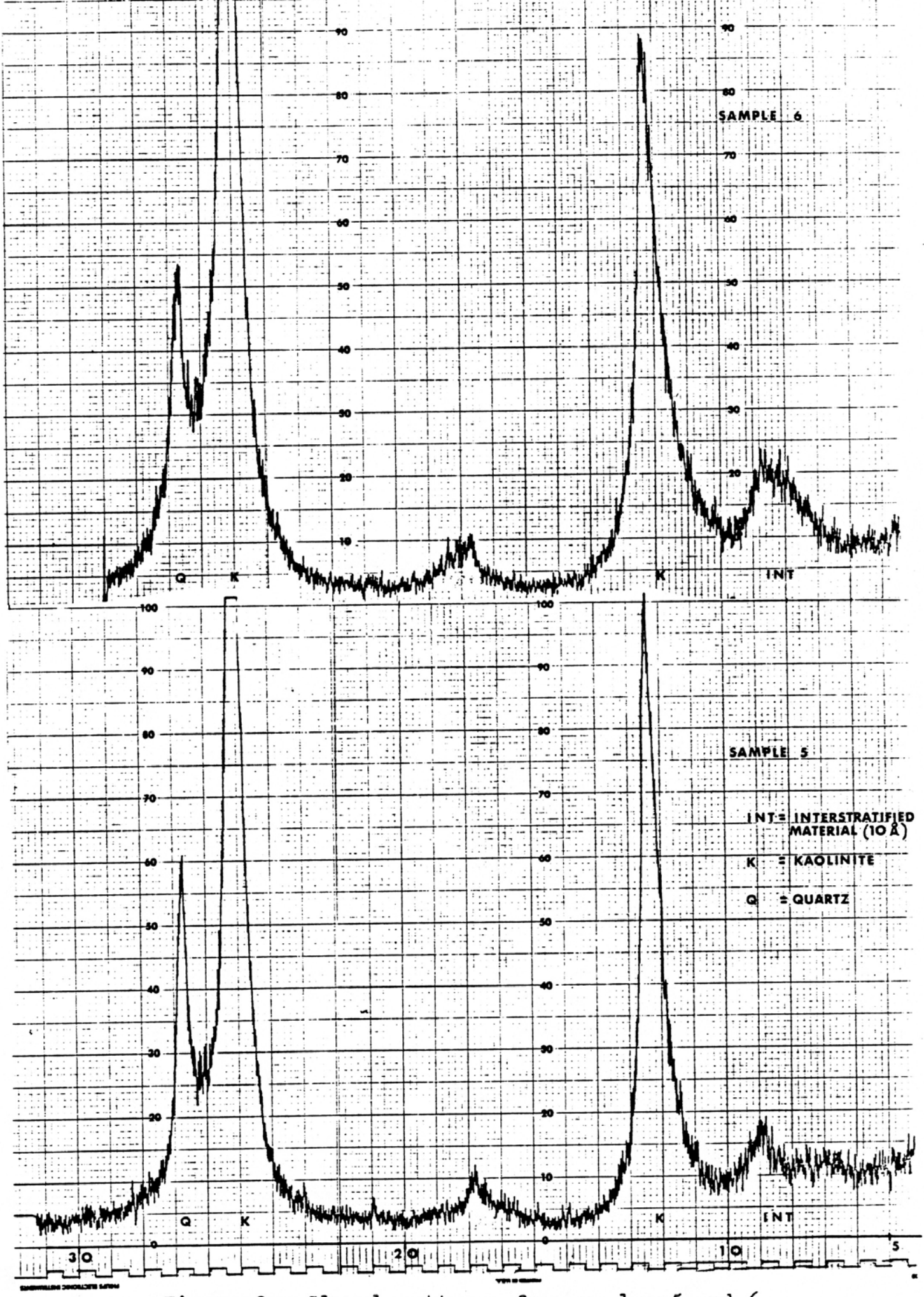

Figure 3e Glycol patterns for samples 5 and 6.

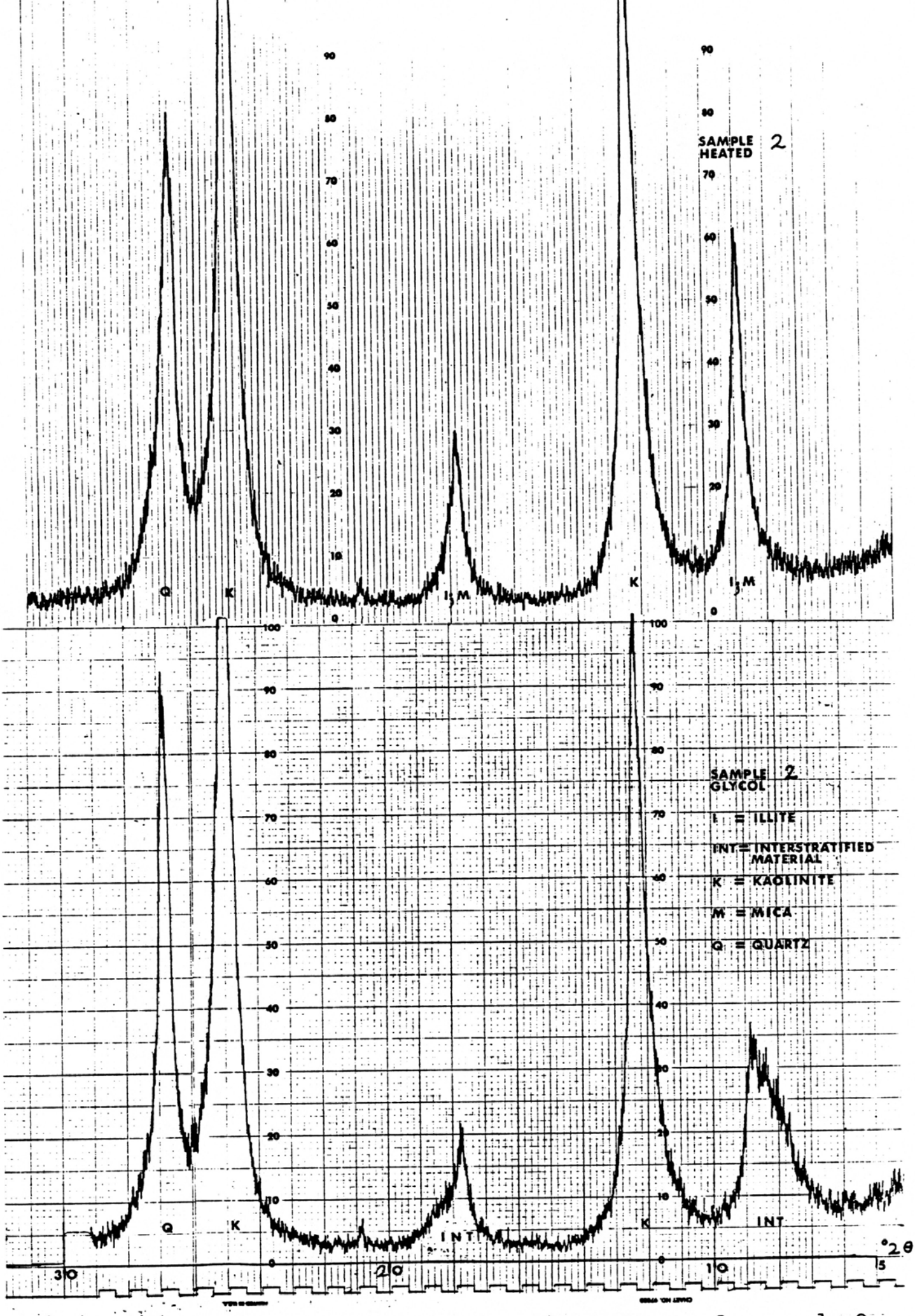

Figure 3f Glycol and heated air-dried patterns for sample 2.

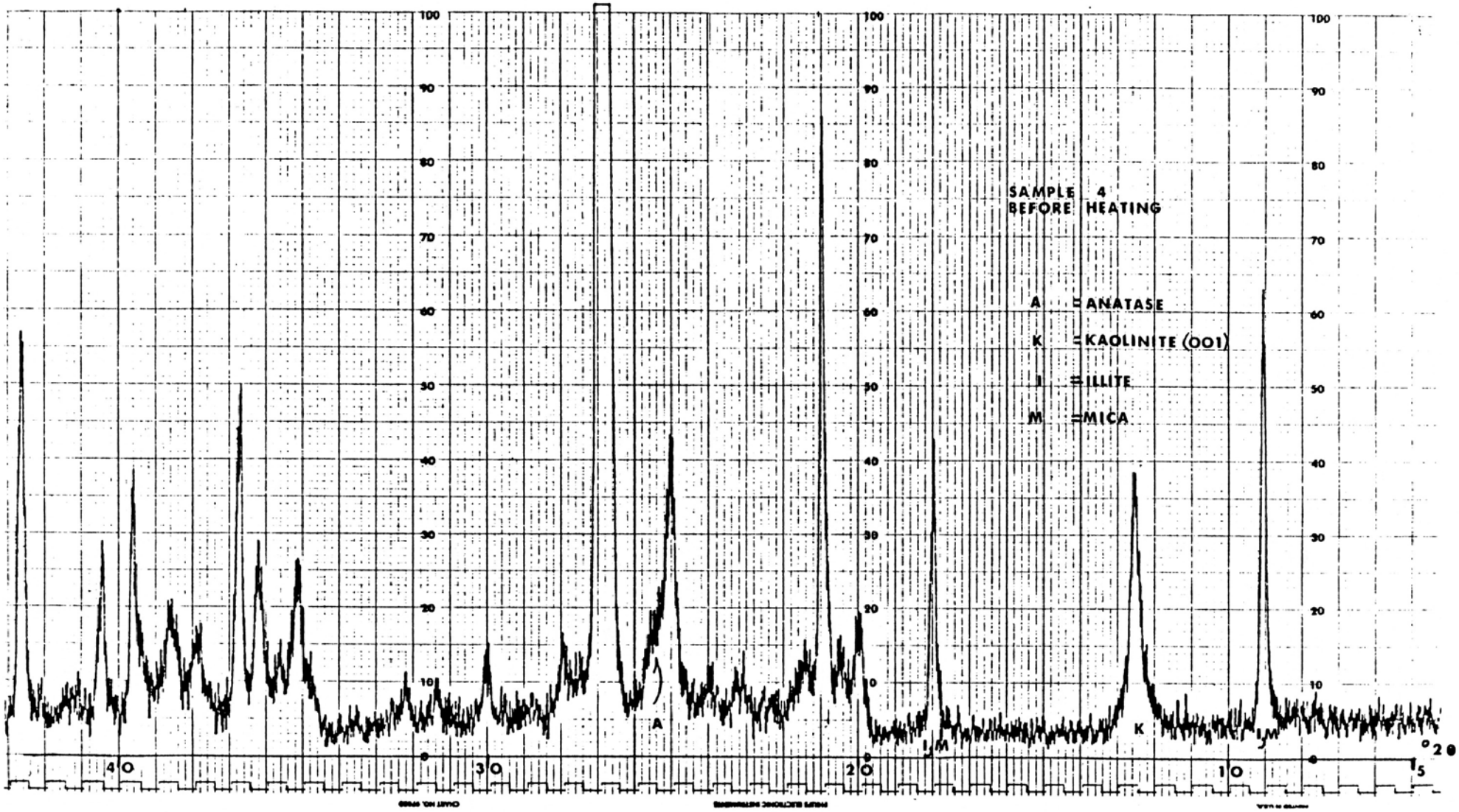

Figure 3g powder pattern (whole fraction) for sample 4 before heating to 600°C.

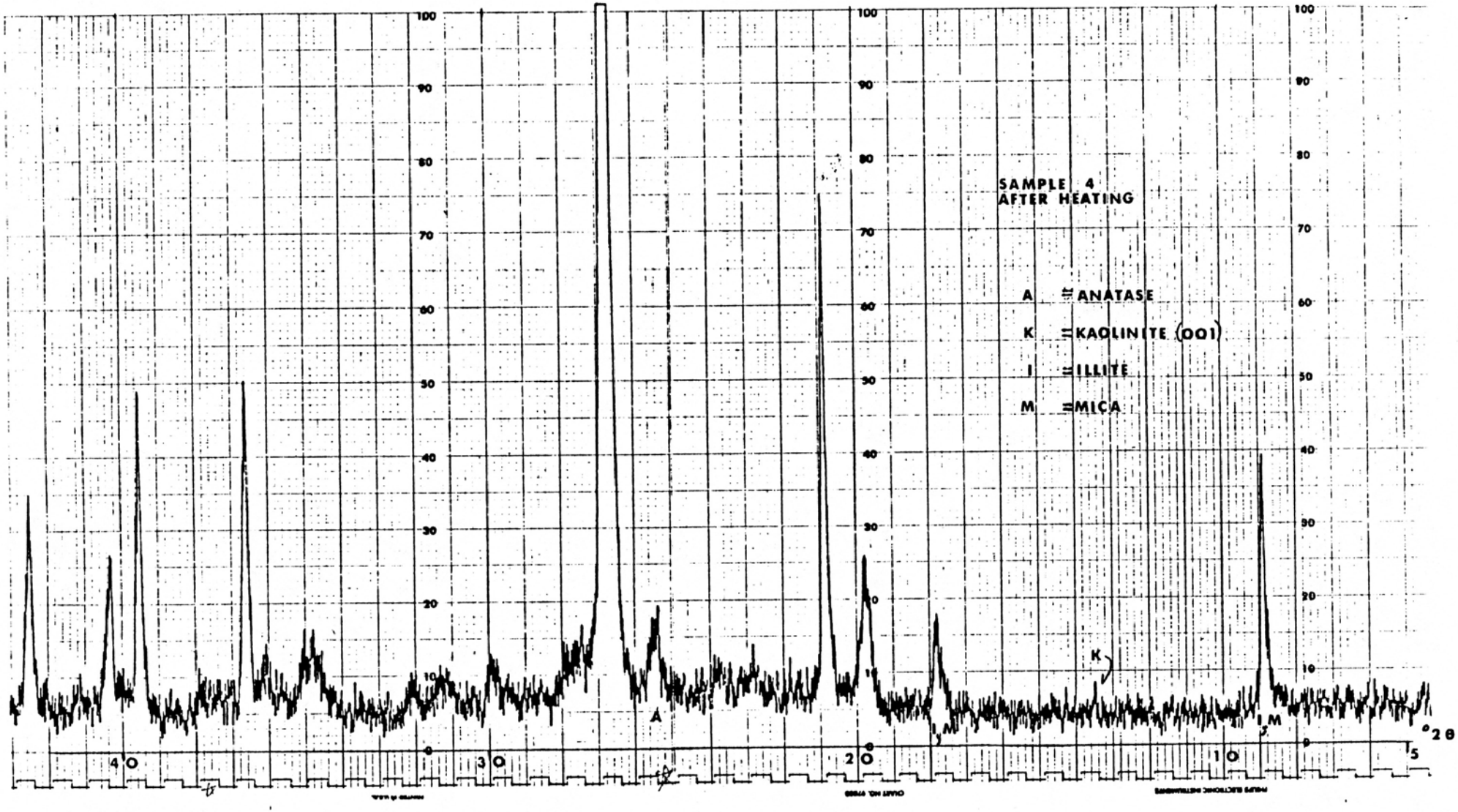

Figure 3h Powder pattern (whole fraction) for sample 4 after heating to 600°C.

CHAPTER V

DISCUSSION

Six clay specimens were taken from a small strip mine in Jackson county, Ohio for X-ray analysis to determine their mineralogic content. Four of the specimens represent material in place near the base of the Lower Kittanning Underclay. The other two samples were obtained from the base of a waste hill, and are unlikely to exemplify material in place. All samples had been exposed to weathering for at least thirty-five years.

Kaolinite, illite, mica (muscovite), quartz, and interstratified material of the 10 Å phase were common to all six samples. Minor TiO_2 in the form of anatase was also present. Hand specimens of sample 4 which were observed to be sandy and micaceous support the idea that they represent the basal material of the Lower Kittanning Underclay.

Grim and Allen (1938) and Schultz (1958) have reported that Pennsylvanian underclays commonly grade into sandy and micaceous shales and sandstones. Schultz (1958) has also found that underclays consist principally of poorly crystallized kaolinite, illite, mixed-layered illite-montmorillonite, and quartz. Comparable clay mineralogy was observed in the diffraction patterns of this study, but whether or not the interstratified expandable material was montmorillonite could not be determined. If montmorillonite was in fact present in

the mixed-layered material associated with illite, its 17 Å phase after glycolation was obscured, since it was not detected in the diffraction patterns.

The presence of titanium dioxide as anatase is in agreement with the study by Calmer (1971), who has analysed numerous specimens taken from the Lower Kittanning Underclay. Yet Calmer states that this disagrees with the findings of others who identified the TiO_2 as rutile.

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